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Immobilization of Rhodium Complexes at Thiolate Monolayers on Gold Surfaces: Catalytic and Structural Studies

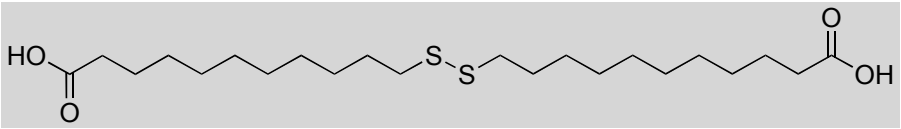
Thomas Belser[†], Meike Stöhr[‡,] and Andreas Pfaltz[†,]**

Contribution from the Department of Chemistry,[†] St. Johanns-Ring 19 and the Department of Physics,[‡] Klingelbergstrasse 82, University of Basel, 4056 Basel (Switzerland).

SUPPORTING INFORMATION

General Methods: Reactions with air- or moisture-sensitive compounds were performed under argon using standard Schlenk techniques or under purified N_2 in a MBraun glovebox. Glasware was oven dried and flame dried prior to use. All chemicals were purchased from Fluka or Aldrich. CH_2Cl_2 was dried over CaH_2 and THF over Na/K and freshly distilled under a stream of nitrogen prior to use. Optical rotations were measured in a Perkin Elmer Polarimeter 341, sodium lamp, 1 dm cuvette length, *c* in g/100 mL. ^{1}H-, ^{13}C-, ^{19}F- and ^{31}P-NMR spectra were recorded in CD_2Cl_2 or $CDCl_3$ on a Bruker Avance 400 MHz or 500 MHz spectrometer and coupling constants are reported in Hz. Chemical shifts are given in ppm relative to TMS. IR spectra: 1600 Perkin Elmer Series FT-IR spectrometer; FAB mass spectra: Finnigan MAT 312; EI mass spectra: VG 70 SE. Elemental analysis were carried out on a Leco CHN-900 and Leco RO-478. Chromatographic purifications were performed by flash chromatography using silica gel (Merck 0.040 - 0.063 mm). Yields for final products refer to isolated products and are the average of three runs. GC analyses: Carlo Erba HRGC Mega2 Series MFC 800 (column: Restek Rtx-1701; 0.25 mm, 30 m, 60 kPa He). HPLC analyses: Shimadzu VP-system (column: Daicel OD-H; 4.6 × 250 mm).

Synthesis of 11-(10'-carboxy-decyldisulfanyl)undecanoic acid



Sodium hydroxide (366 mg, 9.16 mmol), potassium iodide (50.0 mg, 0.30 mmol) and iodine (1.16 g, 4.58 mmol) were added to a solution of 11-mercaptoundecanoic acid (2.00 g, 9.16 mmol) in methanol (50 mL) and the solution was stirred for 30 min. The brown reaction mixture was decolored with a saturated sodium sulfite solution, the solvents concentrated under reduced pressure, the precipitate dissolved in CH_2Cl_2 (50 mL) and the resulting solution washed with a HCl solution (1 M, 50 mL) and water (50 mL). The organic phase was dried over $MgSO_4$, filtered and concentrated under reduced

pressure. Purification of the crude material by crystallization (hexanes/AcOEt) gave 63% yield of the desired 11-(10'-carboxy-decyldisulfanyl)undecanoic acid (1.25 g).

m.p.: 68 - 70 °C. R_f = 0.30 (hexanes/AcOEt = 4:1).

^{1}H-NMR (400.1 MHz, $CDCl_3$, 295 K): δ = 1.28 (s_b, 20 H, CH_2), 1.35 (m_c, 4 H, CH_2), 1.64 (m_c, J = 7.4 Hz, 8 H, CH_2CH$_2$CO$_2$H + SCH$_2$CH_2), 2.34 (t, J = 7.4 Hz, 4 H, CH_2CO$_2$H), 2.68 (t, J = 7.4 Hz, 4 H, SCH_2), 10.98 (s_b, 2 H, CO$_2$*H*).

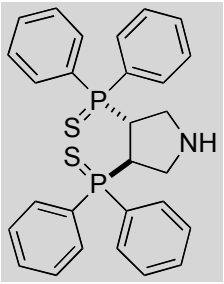
^{13}C{^{1}H}-NMR (100.6 MHz, $CDCl_3$, 295 K): δ = 25.0 (*C*H$_2$), 28.9 (*C*H$_2$), 29.4 (*C*H$_2$), 29.5 (*C*H$_2$), 29.5 (*C*H$_2$), 29.6 (*C*H$_2$), 29.7 (*C*H$_2$), 29.8 (*C*H$_2$), 34.4 (*C*H$_2$), 39.6 (S*C*H$_2$), 180.7 (*C*O$_2$H).

IR (KBr): ν (cm^{-1}) = 2918s, 2849s, 1696s_b, 1471m, 1427m, 1289m, 1261m, 1231m, 1206m, 944m.

MS (FAB): *m/z* (rel int %) = 434 (M^+, 30), 417 (20), 344 (34), 328 (15), 232 (13), 171 (15), 127 (14), 111 (27), 101 (25), 87 (57), 81 (32), 69 (49), 55 (100), 43 (47).

Elemental analysis for $C_{22}H_{42}O_4S_2$ calc.: C 60.79%, H 9.74%, O 14.72%; found: C 60.84%, H 9.68%, O 14.74%.

Synthesis of (3*R*,4*R*)-3,4-bis(diphenylphosphorothioyl)pyrrolidine



Sulfur (0.27 g, 8.40 mmol) was added to a solution of PYRPHOS (1.85 g, 4.20 mmol) in freshly distilled toluene (50 mL) and the reaction mixture was stirred for 12 hours at 23 °C. The resulting solution was concentrated under reduced pressure. Purification of the crude material by flash chromatography, eluting with diethyl ether, gave 95% yield of the desired compound (2.01 g).

m.p.: 212 - 214 °C. $[\alpha]_D^{20}$ = +12.3 (c = 0.80, $CHCl_3$). R_f = 0.50 (diethyl ether).

^{1}H-NMR (400.1 MHz, $CDCl_3$, 295 K): δ = 2.59 (s_b, 1 H, N*H*), 3.12 (m_c, 2 H, NCH_2), 3.27 (m_c, 2 H, NCH_2), 4.01 (m_c, 2 H, PC*H*), 7.00 (m_c, 4 H, CH_{Ph}), 7.17 (m_c, 2 H, CH_{Ph}), 7.42 (m_c, 6 H, CH_{Ph}), 7.60 (m_c, 4 H, CH_{Ph}), 7.88 (m_c, 4 H, CH_{Ph}).

^{13}C{^{1}H}-NMR (100.6 MHz, $CDCl_3$, 295 K): δ = 39.3 - 40.1 (dd, P*C*H), 53.1 (N*C*H$_2$), 128.3 - 128.8 (m, *C*H$_{Ph\text{-}meta}$), 130.0 - 132.9 (m, *C*$_{Ph\text{-}ipso}$), 130.9 - 131.6 (m, *C*H$_{Ph\text{-}ortho\text{ and }para}$).

^{31}P{^{1}H}- NMR (162.0 MHz, $CDCl_3$, 295 K): δ = 51.2 (s).

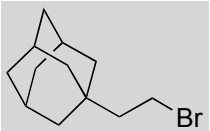
IR (KBr): ν (cm^{-1}) = 3300m, 3048m, 2898m, 1479m, 1435s, 1311m, 1233w, 1158m, 1099s, 998m, 861s, 745s, 718s, 693s, 646s, 605m, 566m, 521s, 503s, 489s.

MS (FAB): *m/z* (rel int %) = 504 ($[M + H]^+$, 30), 286 (9), 217 (15), 185 (6), 77 (5), 68 (100), 39 (5).

Elemental analysis for $C_{28}H_{27}NP_2S_2$ calc.: C 66.78%, H 5.40%, N 2.78%; found: C 66.72%, H 5.32%, N 2.75%.

SYNTHESIS OF THE SPACERS FOR THE GOLD COLLOIDS

Synthesis of 1-(2'-bromo-ethyl)adamantane



N-Bromosuccinimide (987 mg, 5.55 mmol) and triphenylphosphine (1.46 g, 5.55 mmol) were added to a solution of 2-adamant-1-yl-ethanol (1.00 g, 5.55 mmol) in freshly distilled benzene (20 mL) and the reaction mixture was stirred for 12 hours at 23 °C. The resulting solution was washed with a saturated NaCl solution (20 mL) and water (20 mL). The organic phase was dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the crude material by flash chromatography, eluting with *n*-pentane, gave 92% yield of 1-(2'-bromo-ethyl)adamantane (1.24 g).

m.p.: 66 - 68 °C. R_f = 0.78 (*n*-pentane).

^{1}H-NMR (400.1 MHz, $CDCl_3$, 295 K): δ = 1.51 (m_c, J = 2.5 Hz, 6 H, CC$H_{2\text{-Ad}}$), 1.61 - 1.70 (m, 6 H, C$H_{2\text{-Ad}}$), 1.72 (m_c, 2 H, BrCH$_2$CH_2), 1.96 (m_c, 3 H, CH_{Ad}), 3.40 (m_c, 2 H, BrCH_2).

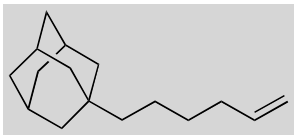
^{13}C{^{1}H}-NMR (100.6 MHz, $CDCl_3$, 295 K): δ = 28.6 (*C*H$_{\text{Ad}}$), 29.2 (Br*C*H$_2$), 34.1 (*C*$_{\text{Ad}}$), 37.1 (*C*H$_{2\text{-Ad}}$), 42.2 (C*C*H$_{2\text{-Ad}}$), 48.2 (BrCH$_2$*C*H$_2$).

IR (KBr): ν (cm^{-1}) = 2896s, 2843s, 2652w, 1452s, 1442m, 1344m, 1329m, 1312m, 1256m, 1215m, 1094m, 973m, 810m, 746w, 719m, 658m, 560s.

MS (EI): *m/z* (rel int %) = 242 (M$^+$, 1, ^{79}Br), 135 (100), 107 (6), 93 (13), 79 (15), 67 (6), 55 (3), 41 (6).

Elemental analysis for $C_{12}H_{19}Br$ calc.: C 59.27%, H 7.88%; found: C 59.22%, H 7.79%.

Synthesis of 1-(hex-5'-enyl)adamantane



3-Butenylmagnesium bromide solution (0.5 M in THF, 94 mL, 47.0 mmol) was added tropwise at -78 °C to a solution of 1-(2'-bromo-ethyl)adamantane (5.00 g, 20.6 mmol) in freshly distilled THF (30 mL). After 10 min, a lithium tetrachlorocuprate(II) solution (0.1 M in THF, 2.10 mL, 0.21 mmol) was added and the reaction mixture was stirred for 2 hours at -78 °C and slowly warmed up to 23 °C over 12 hours. The resulting solution was washed with a saturated NH_4Cl solution (100 mL) and water (100 mL). The organic phase was dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the crude material by flash chromatography, eluting with *n*-pentane, gave 92% yield of 1-(hex-5'-enyl)adamantane (4.13 g).

R_f = 0.86 (hexanes).

^{1}H-NMR (400.1 MHz, $CDCl_3$, 295 K): δ = 1.03 (t, J = 7.1 Hz, 2 H, CCH_2), 1.24 (quin, J = 7.1 Hz, 2 H, CCH$_2$CH_2), 1.33 (quin, J = 7.1 Hz, 2 H, CCH$_2$CH$_2$CH_2), 1.45 (m_c, J = 2.2 Hz, 6 H, CC$H_{2\text{-Ad}}$), 1.66

(m_c, 6 H, C$H_{2\text{-Ad}}$), 1.93 (m_c, 3 H, CH_{Ad}), 2.05 (m_c, 2 H, CCH$_2$CH$_2$CH$_2$CH_2) 4.96 (m_c, 2 H, C$H_{2\text{-vinyl}}$), 5.81 (m_c, 1 H, CH_{vinyl}).

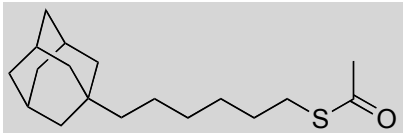
^{13}C{^{1}H}-NMR (100.6 MHz, $CDCl_3$, 295 K): δ = 22.0 (*C*H$_2$), 28.9 (*C*H$_{\text{Ad}}$), 30.0 (*C*H$_2$), 32.4 (C_{Ad}), 34.0 (*C*H$_2$), 37.4 (*C*H$_{2\text{-Ad}}$), 42.7 (C*C*H$_{2\text{-Ad}}$), 44.7 (*C*H$_2$), 114.2 (*C*H$_{2\text{-vinyl}}$), 139.4 (*C*H$_{\text{vinyl}}$).

IR (NaCl): ν (cm^{-1}) = 3076w, 2898s, 2845s, 2656w, 1820w, 1640m, 1450m, 1098w, 991m, 908m.

MS (EI): *m/z* (rel int %) = 218 (M$^+$, 3), 135 (100), 107 (4), 93 (8), 79 (9), 67 (5), 55 (4), 41 (5).

Elemental analysis for $C_{16}H_{26}$ calc.: C 88.00%, H 12.00%; found: C 88.07%, H 12.01%.

Synthesis of thioacetic acid (*S*)-6-(adamant-1'-yl)hexyl ester



Thioacetic acid (4.21 mL, 58.9 mmol) was added to a solution of 1-(hex-5'-enyl)adamantane (5.00 g, 22.9 mmol) in freshly distilled THF (250 mL) and cooled to 20 °C with a cryostate (cooling bath: H_2O/EtOH = 80:20). The solution was irradiated during 7 hours with a 300 W lamp (Osram Ultra-Vitalux 300 W). During that time was added 2,2'-azobisisobutyronitrile (900 mg, 5.48 mmol) in freshly distilled THF (20 mL) with a syringe pump. Irradiation was continued for another 4 hours. The solvent was concentrated under reduced pressure and the residue dissolved in dichloromethane (100 mL). The resulting solution was washed with a saturated Na_2CO_3 solution (100 mL) and water (100 mL). The organic phase was dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the crude material by flash chromatography, eluting with 5% diethyl ether in *n*-pentane, gave 82% yield of thioacetic acid (*S*)-6-(adamant-1'-yl)hexyl ester (5.50 g).

R_f = 0.67 (*n*-pentane/diethyl ether = 20:1).

^{1}H-NMR (400.1 MHz, $CDCl_3$, 295 K): δ = 1.00 (t, *J* = 7.3 Hz, 2 H, CCH_2), 1.22 (m_c, 4 H, CH_2), 1.35 (quin, *J* = 7.3 Hz, 2 H, CCH$_2$CH_2), 1.43 (m_c, *J* = 2.3 Hz, 6 H, CC$H_{2\text{-Ad}}$), 1.55 (quin, *J* = 7.3 Hz, 2 H, CH_2CH$_2$S), 1.64 (m_c, 6 H, C$H_{2\text{-Ad}}$), 1.92 (m_c, 3 H, CH_{Ad}), 2.31 (s, 3 H, SCOCH_3), 2.85 (t, *J* = 7.3 Hz, 2 H, CH_2S).

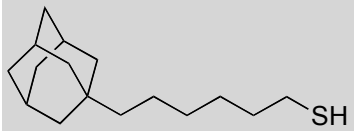
^{13}C{^{1}H}-NMR (100.6 MHz, $CDCl_3$, 295 K): δ = 22.3 (*C*H$_2$), 28.8 (*C*H$_{\text{Ad}}$), 29.0 (*C*H$_2$), 29.3 (*C*H$_2$), 29.6 (*C*H$_2$), 30.2 (*C*H$_2$), 30.7 (*C*H$_3$), 32.3 (C_{Ad}), 37.4 (*C*H$_{2\text{-Ad}}$), 42.6 (C*C*H$_{2\text{-Ad}}$), 44.7 (*C*H$_2$), 196.1 (S*C*O).

IR (NaCl): ν (cm^{-1}) = 2902s, 2847s, 2661w, 1694s, 1450m, 1352m, 1132m, 954m, 864w, 624w.

MS (EI): *m/z* (rel int %) = 294 (M$^+$, 4), 251 (5), 135 (100), 107 (5), 93 (9), 79 (10), 43 (15).

Elemental analysis for $C_{18}H_{30}OS$ calc.: C 73.41%, H 10.27%, O 5.43%; found: C 73.21%, H 10.14%, O 5.57%.

Synthesis of 6-(adamant-1'-yl)hexanethiol



Conc. HCl (37%, 425 mL, 5.18 mmol) was added to a solution of thioacetic acid (*S*)-6-(adamant-1'-yl)-hexyl ester (150 mg, 509 mmol) in methanol (5 mL) and the reaction mixture was stirred for 10 hours at 65 °C. The solvent was concentrated under reduced pressure and the residue dissolved in diethyl ether (20 mL). The resulting solution was washed with a HCl solution (1 M, 20 mL) and water (20 mL). The organic phase was dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the crude material by flash chromatography, eluting with *n*-pentane, gave 86% yield of 6-(adamant-1'-yl)-hexanethiol (0.11 g).

R_f = 0.65 (*n*-pentane).

^{1}H-NMR (400.1 MHz, $CDCl_3$, 295 K): δ = 1.01 (t, J = 7.4 Hz, 2 H, CCH_2), 1.22 (m_c, 4 H, CH_2), 1.32 (t, J = 7.7 Hz, 1 H, S*H*), 1.38 (quin, J = 7.4 Hz, 2 H, CCH_2CH_2), 1.44 (m_c, J = 2.5 Hz, 6 H, CC$H_{2\text{-Ad}}$), 1.60 (quin, J = 7.4 Hz, 2 H, CH_2CH_2SH), 1.64 (m_c, 6 H, C$H_{2\text{-Ad}}$), 1.92 (m_c, 3 H, CH_{Ad}), 2.51 (q, J = 7.4 Hz, 2 H, CH_2SH).

^{13}C{^{1}H}-NMR (100.6 MHz, $CDCl_3$, 295 K): δ = 22.3 (CH_2), 24.8 (CH_2), 28.5 (CH_2), 28.9 (CH_{Ad}), 30.1 (CH_2), 32.3 (C_{Ad}), 34.2 (CH_2), 37.4 (CH_2), 42.6 (CH_{Ad}), 44.8 (CH_2).

IR (NaCl): ν (cm^{-1}) = 2902s, 2846s, 2663w, 1450m, 1347w, 1101w.

MS (EI): *m/z* (rel int %) = 252 (M^+, 3), 135 (100), 93 (11), 79 (11), 67 (6), 41 (6).

Elemental analysis for $C_{16}H_{28}S$ calc.: C 76.12%, H 11.18%; found: C 76.07%, H 11.08%.

Synthesis of 11-aminoundecanol

11-Aminoundecanoic acid (21.0 g, 102 mmol) was added slowly at -20 °C to a solution of $LiAlH_4$ (5.20 g, 137 mmol) in freshly distilled THF (200 mL) and the reaction mixture was stirred for 6 hours at 67 °C. The solution was cooled to 0 °C, treated with a NaOH solution (10%, 10 mL) and H_2O (20 mL) and stirred for 30 min at 23 °C. The reaction mixture was dried over $MgSO_4$, filtered and concentrated under reduced pressure to provide the desired 11-aminoundecanol (10.3 g) in 53% yield.

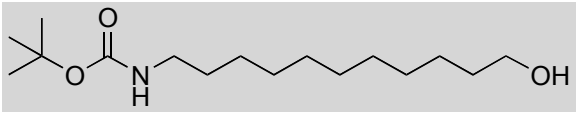
m.p.: 66 - 68 °C.

^{1}H-NMR (400.1 MHz, CD_2Cl_2, 295 K): δ = 1.27 (s_b, 14 H, CH_2), 1.39 (quin, J = 7.0 Hz, 2 H, C$H_2CH_2NH_2$), 1.50 (quin, J = 6.5 Hz, 2 H, CH_2CH_2OH), 2.61 (t, J = 7.0 Hz, 2 H, CH_2NH_2), 3.54 (t, J = 6.5 Hz, 2 H, CH_2OH) $\Rightarrow$ O*H* und NH_2 signals lies under the quintetts between 1.36 - 1.54 Hz.

^{13}C{^{1}H}-NMR (100.6 MHz, CD_2Cl_2, 295 K): δ = 25.9 (CH_2), 27.0 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.7 (CH_2), 29.7 (CH_2), 33.0 (CH_2CH_2OH), 34.1 ($CH_2CH_2NH_2$), 42.3 (CH_2NH_2), 62.7 (CH_2OH).

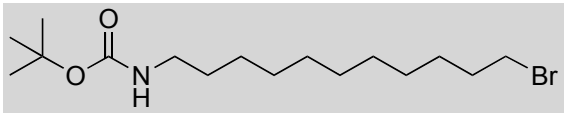
IR (KBr): ν (cm^{-1}) = 3338m, 3086m$_b$, 2923s, 2849s, 1614w, 1472m, 1348m, 1077m, 1031m, 991m.
MS (FAB): *m/z* (rel int %) = 188 ($[M + H]^+$, 100), 69 (10), 55 (19), 44 (9), 41 (9).
Elemental analysis for $C_{11}H_{25}NO$ calc.: C 70.53%, H 13.45%, N 7.48%; found: C 70.69%, H 13.43%, N 7.35%.

Synthesis of *tert*-butyl 11-hydroxyundecylcarbamate



Triethylamine (9.00 mL, 64.7 mmol) and di-*tert*-butyl dicarbonate (14.1 g, 64.6 mmol) were added at 0 °C to a solution of 11-aminoundecanol (12.0 g, 64.1 mmol) in freshly distilled CH_2Cl_2 (200 mL) and the reaction mixture was stirred for 2 hours at 0 °C and another 8 hours at 23 °C. The resulting solution was washed with a saturated NaCl solution (100 mL) and water (100 mL). The organic phase was dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the crude material by flash chromatography, eluting with 30% AcOEt in hexanes, gave 89% yield of *tert*-butyl 11-hydroxyundecylcarbamate (16.3 g).
m.p.: 34 - 36 °C. R_f = 0.38 (hexanes/AcOEt = 2:1).
^{1}H-NMR (400.1 MHz, $CDCl_3$, 295 K): δ = 1.25 (s_b, 10 H, CH_2), 1.30 (m_c, 4 H, CH_2), 1.42 (s_b, 11 H, C(CH_3)$_3$ + CH_2CH$_2$NH), 1.54 (m_c, 3 H, O*H* + CH_2CH$_2$OH), 3.08 (m_c, *J* = 6.3 Hz, 6.6 Hz, 2 H, CH_2NH), 3.61 (m_c, *J* = 5.6 Hz, 6.3 Hz, 2 H, CH_2OH), 4.54 (s_b, 1 H, N*H*).
^{13}C{^{1}H}-NMR (100.6 MHz, $CDCl_3$, 295 K): δ = 25.8 (*C*H$_2$), 26.8 (*C*H$_2$), 28.5 (C(*C*H$_3$)$_3$), 29.3 (*C*H$_2$), 29.5 (*C*H$_2$), 29.5 (*C*H$_2$), 29.6 (*C*H$_2$), 29.6 (*C*H$_2$), 30.1 (*C*H$_2$CH$_2$NH), 32.8 (*C*H$_2$CH$_2$OH), 40.7 (*C*H$_2$NH), 63.1 (*C*H$_2$OH), 79.1 (*C*(CH$_3$)$_3$), 156.1 (*C*O).
IR (NaCl): ν (cm^{-1}) = 3353m$_b$, 2926s, 2854m, 1693s, 1526m$_b$, 1366m, 1275m, 1251m, 1173s.
MS (FAB): *m/z* (rel int %) = 288 ($[M + H]^+$, 3), 232 (7), 188 (17), 74 (12), 69 (11), 57 (100), 41 (26).
Elemental analysis for $C_{16}H_{33}NO_3$ calc.: C 66.86%, H 11.57%, N 4.87%; found: C 66.95%, H 11.49%, N 4.79%.

Synthesis of *tert*-butyl 11-bromoundecylcarbamate



N-Bromosuccinimide (10.0 g, 56.2 mmol) and triphenylphosphine (14.8 g, 56.4 mmol) were added to a solution of *tert*-butyl 11-hydroxyundecylcarbamate (16.0 g, 55.7 mmol) in freshly distilled benzene (200 mL) and the reaction mixture was stirred for 12 hours at 23 °C. The resulting solution was washed with a saturated NaCl solution (200 mL) and water (200 mL). The organic phase was dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification by flash chromatography, eluting with 10% AcOEt in hexanes, gave 74% yield of *tert*-butyl 11-bromoundecylcarbamate (14.5 g).

m.p.: 60 - 62 °C. R_f = 0.37 (hexanes/AcOEt = 10:1).

^{1}H-NMR (400.1 MHz, $CDCl_3$, 295 K): δ = 1.25 (s_b, 12 H, CH_2), 1.42 (s_b, 13 H, CH_2CH$_2$CH$_2$Br + C(CH_3)$_3$ + CH_2CH$_2$NH), 1.83 (m_c, J = 6.9 Hz, 7.2 Hz, 2 H, CH_2CH$_2$Br), 3.08 (t, J = 6.6 Hz, 2 H, CH_2NH), 3.38 (t, J = 6.9 Hz, 2 H, CH_2Br), 4.53 (s_b, 1 H, N*H*).

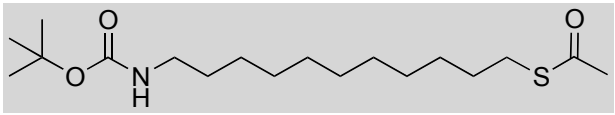
^{13}C{^{1}H}-NMR (100.6 MHz, $CDCl_3$, 295 K): δ = 26.8 (*C*H$_2$), 28.2 (*C*H$_2$), 28.5 (C(*C*H$_3$)$_3$), 28.8 (*C*H$_2$), 29.3 (*C*H$_2$), 29.4 (*C*H$_2$), 29.5 (*C*H$_2$), 29.5 (*C*H$_2$), 30.1 (*C*H$_2$CH$_2$NH), 32.9 (*C*H$_2$CH$_2$Br), 34.1 (*C*H$_2$Br), 40.7 (*C*H$_2$NH), 79.0 (*C*(CH$_3$)$_3$), 156.0 (*C*O).

IR (KBr): ν (cm^{-1}) = 3377s, 2918s, 2851s, 1687s_b, 1522s_b, 1469m, 13$\overline{7}$4m, 1280m, 1237m, 1170m_b, 1026w, 976w, 870m, 720m, 643m.

MS (FAB): *m/z* (rel int %) = 350 (M^+, 4, ^{79}Br), 294 (96, ^{79}Br), 250 (13, ^{79}Br), 214 (8), 137 (8), 74 (41), 57 (100), 41 (20).

Elemental analysis for $C_{16}H_{32}BrNO_2$ calc.: C 54.85%, H 9.21%, N 3.91%; found: C 55.01%, H 9.06%, N 3.89%.

Synthesis of (*S*)-11-(*tert*-butoxycarbonyl)undecylethanethioate



Thioacetic acid (4.00 mL, 56.0 mmol), triethylamine (8.00 mL, 57.5 mmol) and 4-DMAP (0.50 g, 4.10 mmol) were added to a solution of *tert*-butyl 11-bromoundecylcarbamate (14.5 g, 41.4 mmol) in freshly distilled CH_2Cl_2 (200 mL) and the reaction mixture was stirred for 24 hours at 23 °C. The solution was washed with a saturated Na_2CO_3 solution (200 mL) and water (200 mL). The organic phase was dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the crude material by flash chromatography, eluting with 10% AcOEt in hexanes and subsequent crystallization (*n*-pentane), gave 79% yield of (*S*)-11-(*tert*-butoxycarbonyl)undecyl-ethanethioate (11.3 g).

m.p.: 64 - 66 °C. R_f = 0.25 (hexanes/AcOEt = 10:1).

^{1}H-NMR (400.1 MHz, $CDCl_3$, 295 K): δ = 1.22 (s_b, 10 H, CH_2), 1.25 (m_c, 2 H, NCH$_2$CH$_2$CH_2), 1.30 (m_c, 2 H, CH_2CH$_2$CH$_2$S), 1.41 (s_b, 11 H, C(CH_3)$_3$ + NCH$_2$CH_2), 1.52 (m_c, J = 6.8 Hz, 7.4 Hz, 2 H, CH_2CH$_2$S), 2.29 (s, 3 H, SCOCH_3), 2.83 (t, J = 7.4 Hz, 2 H, CH_2S), 3.07 (t, J = 6.6 Hz, 2 H, NCH_2), 4.55 (s_b, 1 H, N*H*).

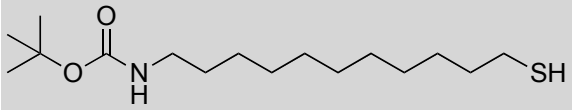
^{13}C{^{1}H}-NMR (100.6 MHz, $CDCl_3$, 295 K): δ = 26.8 (NCH$_2$CH$_2$*C*H$_2$), 28.5 (C(*C*H$_3$)$_3$), 28.8 (*C*H$_2$S), 29.1 (*C*H$_2$), 29.2 (*C*H$_2$), 29.3 (*C*H$_2$CH$_2$S), 29.4 (*C*H$_2$), 29.5 (*C*H$_2$), 29.5 (*C*H$_2$), 29.5 (*C*H$_2$), 30.1 (NCH$_2$*C*H$_2$), 30.7 (SCO*C*H$_3$), 40.6 (N*C*H$_2$), 78.9 (*C*(CH$_3$)$_3$), 156.0 (*C*O), 196.0 (S*C*O).

IR (KBr): ν (cm^{-1}) = 3380m, 2918m, 2851m, 1687s_b, 1522s_b, 1469m, 1364m, 1282m, 1238m, 1172m, 1138m, 1116m, 1000w, 959m, 870w, 720w, 639m.

MS (FAB): *m/z* (rel int %) = 346 ([M + H]$^+$, 24), 290 (26), 246 (100), 230 (9), 202 (9), 57 (55), 43 (31).

Elemental analysis for $C_{18}H_{35}NO_3S$ calc.: C 62.56%, H 10.20%, N 4.05%; found: C 62.56%, H 10.16%, N 4.08%.

Synthesis of *tert*-butyl 11-mercaptoundecylcarbamate



A hydrazine solution (1 M in THF, anhydrous, 30.0 mL, 30.0 mmol) was added at 0 °C to a solution of (*S*)-11-(*tert*-butoxycarbonyl)undecylethanethioate (1.00 g, 2.90 mmol) in freshly distilled CH_2Cl_2 (20 mL) and the reaction mixture was stirred for 4 hours at 23 °C. The solvent was concentrated under reduced pressure and the residue dissolved in CH_2Cl_2 (50 mL). The resulting solution was washed with a saturated NH_4Cl solution (50 mL) and water (50 mL). The organic phase was dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification by flash chromatography, eluting with 10% AcOEt in hexanes, gave 98% yield of *tert*-butyl 11-mercaptoundecylcarbamate (0.86 g).

m.p.: 52 - 54 °C. R_f = 0.36 (hexanes/AcOEt = 10:1).

^{1}H-NMR (400.1 MHz, $CDCl_3$, 295 K): δ = 1.25 (s_b, 12 H, CH_2), 1.32 (t, J = 7.6 Hz, 1 H, SH), 1.36 (m_c, 2 H, CH_2CH$_2$CH$_2$SH), 1.43 (s_b, 11 H, C(CH_3)$_3$ + NCH$_2$CH_2), 1.59 (quin, J = 7.2 Hz, 2 H, CH_2CH$_2$S), 2.51 (m_c, J = 7.2 Hz, 7.6 Hz, 2 H, CH_2SH), 3.09 (t, J = 6.6 Hz, 2 H, NCH_2), 4.50 (s_b, 1 H, NH).

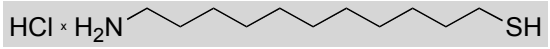
^{13}C{^{1}H}-NMR (100.6 MHz, $CDCl_3$, 295 K): δ = 24.7 (*C*H$_2$SH), 26.9 (*C*H$_2$), 28.4 (*C*H$_2$CH$_2$CH$_2$SH), 28.5 (C(*C*H$_3$)$_3$), 29.1 (*C*H$_2$), 29.3 (*C*H$_2$), 29.5 (*C*H$_2$), 29.5 (*C*H$_2$), 29.6 (*C*H$_2$), 30.1 (NCH$_2$*C*H$_2$), 34.1 (*C*H$_2$CH$_2$SH), 40.7 (N*C*H$_2$), 79.0 (*C*(CH$_3$)$_3$), 156.0 (*C*O).

IR (KBr): ν (cm^{-1}) = 3373s, 2921s, 2848s, 1682s_b, 1513s_b, 1464m, 1367m, 1284m, 1241m, 1166s_b, 1044w, 1001m, 977m, 864m, 783w, 723m, 580m_b.

MS (FAB): *m/z* (rel int %) = 304 ([M + H]$^+$, 10), 248 (41), 204 (100), 74 (13), 57 (77), 41 (14).

Elemental analysis for $C_{16}H_{33}NO_2S$ calc.: C 63.32%, H 10.96%, N 4.62%, O 10.54%; found: C 63.41%, H 10.90%, N 4.62%, O 10.46%.

Synthesis of 11-aminoundecane-1-thiol hydrochloride



Tert-butyl 11-mercaptoundecylcarbamate (1.00 g, 3.30 mmol) was dissolved in a HCl solution in dioxane (4 M, 20.0 mL, 80 mmol) and the reaction mixture was stirred for 3 hours at 23 °C. The solvent was concentrated under reduced pressure and the solid washed with diethyl ether (50 mL) and *n*-pentane (50 mL) to provide the desired 11-aminoundecane-1-thiol hydrochloride (0.78 g) in 99% yield.

m.p.: 162 - 164 °C.

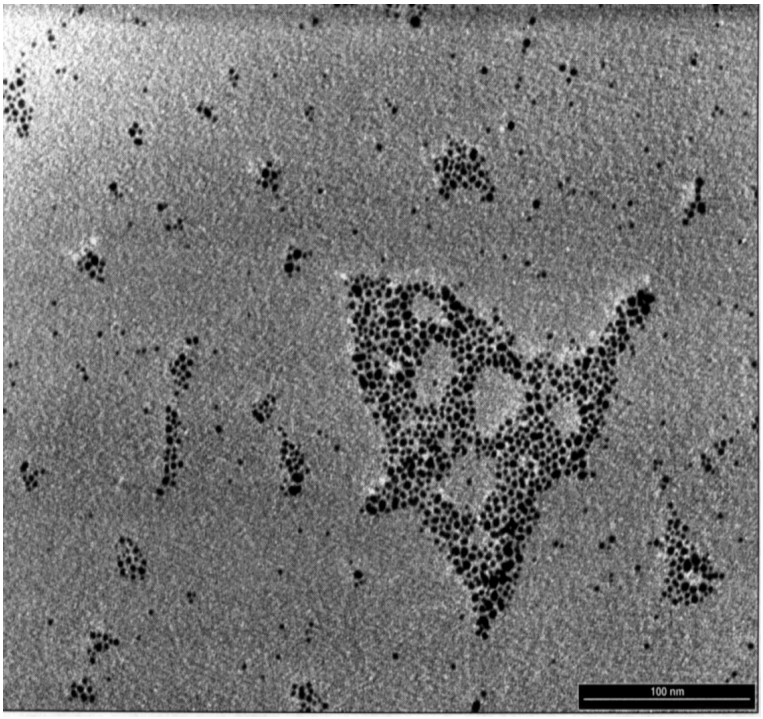
^{1}H-NMR (400.1 MHz, (CD$_3$)$_2$SO, 295 K): δ = 1.25 (s_b, 12 H, CH_2), 1.32 (m_c, 2 H, NCH$_2$CH$_2$CH_2), 1.51 (quin, J = 6.8 Hz, 2 H, CH_2CH$_2$SH), 1.53 (quin, J = 7.4 Hz, 2 H, NCH$_2$CH_2), 2.23 (t, J = 7.6 Hz, 1 H, SH), 2.46 (m_c, J = 6.8 Hz, 7.6 Hz, 2 H, CH_2SH), 2.75 (t_b, J = 7.4 Hz, 2 H, NCH_2), 7.78 (s_b, 3 H, NH_3Cl).

$^{13}C\{^1H\}$-NMR (100.6 MHz, $(CD_3)_2SO$, 295 K): δ = 23.7 (CH_2SH), 25.8 (CH_2), 26.9 (NCH_2CH_2), 27.7 ($NCH_2CH_2CH_2$), 28.5 (CH_2), 28.5 (CH_2), 28.8 (CH_2), 28.9 (CH_2), 28.9 (CH_2), 33.4 (CH_2CH_2SH), 38.7 (NCH_2).
IR (KBr): ν (cm^{-1}) = 2918s_b, 2657m, 2547m, 2021w_b, 1625m, 1511m, 1473m, 1398w, 1308w, 1196w.
MS (FAB): *m/z* (rel int %) = 204 ([M - Chlorid]$^+$, 100), 55 (6).
Elemental analysis for $C_{11}H_{26}ClNS$ calc.: C 55.09%, H 10.93%, N 5.84%; found: C 55.21%, H 10.89%, N 5.73%.

Analyses of thiolate-protected gold colloids

Colloid	d (TEM) [nm]	Elemental analysis
6	2.32 ± 0.46 nm	C 16.52%, S 2.29%, Au 79.5%
7	3.48 ± 0.61 nm	C 7.15%, S 2.38%, Au 90.1%
8	3.44 ± 0.59 nm	C 11.39%, S 2.22%, Au 76.8%
9	2.60 ± 0.43 nm	C 7.39%, N 0.71, S 1.40%, Au 81.5%
10	3.39 ± 0.73 nm	C 8.26%, O 0.83, S 1.79%, Au 79.3%

TEM-image of colloid 7



Complete Reference 13:

[13] M. J. Hostetler, J. E. Wingate, C.-J. Zhong, J. E. Harris, R. W. Vachet, M. R. Clark, J. D. Londono, S. J. Green, J. J. Stokes, G. D. Wignall, G. L. Glish, M. D. Porter, N. D. Evans, R. W. Murray, *Langmuir* **1998**, *14*, 17.